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10/089311
JC15 Rec'd PCT/PTO 27 MAR 2002

FUEL OIL COMPOSITIONS WITH IMPROVED COLD FLOW PROPERTIES

This invention relates to fuel oil compositions, especially middle distillate fuel oil compositions, with improved flow properties.

It is important that fuel oil compositions, especially middle distillate oil compositions such as automotive diesel oils, heating oils and gas oils (hereafter collectively referred to as "fuel oil" for convenience) retain their flow properties at relatively low temperatures. The main cause of such loss of flow properties is due to the formation of wax which tends to precipitate out and agglomerate thereby plugging burner and vehicle fuel filters and hence impairing flow. The temperature at which the wax starts to appear is termed the cloud point of the fuel. The cold filter plugging point (CFPP) is recognised as a measure of the operability of a fuel and the temperature at which a fuel will start to block vehicle filters. It is generally less than or equal to the cloud point of the fuel. This problem has been well recognized in the art and has hitherto been mitigated by the use of various flow improving additives also known as middle distillate flow improvers (MDFI) which reduce the CFPP of responsive fuels. One such example is Paraflow® 240 (commercially sold by Infineum). The flow improvers can change the size or the shape of the crystals as they precipitate out of the oil at low temperatures thereby allowing them to pass through the vehicle filter easily and avoid blockage of the fuel filter of the vehicle. Either way, it is important that the flow properties of the fuel oils are maintained.

Hitherto, crude oil was refined into motor gasoline, automotive diesel oils (hereafter "ADO") and gas oils used as heating oils (fuel oils) and their respective specifications were such that it was possible to easily treat ADO, gasoil and heating oils. However, recent legislation to minimise the amount of sulphur and also constrain other properties, eg density, in ADOs has meant that some of the heavier components of ADOs, such as e.g. catalytically cracked heating oils, have been displaced into the gasoil and heating oil fractions. These changes in the composition of ADO, gasoils and heating oils may mean that the effectiveness of conventional cold flow improvers such as Paraflow® 240 is lessened.

It is an object of the present invention to improve the flow properties of fuel oils (as herein defined) containing conventional flow improvers by incorporating therein a heavy catalytically-cracked naphtha.

Accordingly, the present invention is a fuel oil composition having improved cold-flow properties, said composition comprising a cold flow additive and the following components from various pipestills of a petroleum crude refinery process:

a. A relatively heavy fraction from a catalytically cracked heavy gasoil in turn derived from an atmospheric or vacuum pipestill, said fraction having a boiling range of 170 to 380°C in an amount of 3 to 20% by weight and

b. A gasoil product from an atmospheric pipestill, said product having a boiling range of 225 to 360°C in an amount of 30-50% by weight,

characterized in that components (a) and/or (b) in said composition is at least partially replaced by at least one relatively light naphtha fraction (c) from the atmospheric or vacuum pipestills, said light fraction (c) having a boiling range of 130 to 235°C and being present in an amount of 3 to 20% by weight, all weights being based on the total weight of the fuel oil composition.

In the fuel compositions of the present invention, the various components referred to are all derivable from various process streams of a petroleum crude refinery process. Such methods are well known in the art and are described in detail, for instance, by Keith Owen and Trevor Colley in "Automotive Fuels Reference Book", Second Edition, published by the Society of Automotive Engineers, Inc, Warrendale, PA, USA (1995). Specifically referred to are Chapter 3 of this text-book at pages 29-49 and Chapter 16 at pages 419-469 and 865-890, the latter pages forming Appendix 12 which is a 'Glossary of Terms' used in this art. Thus, reference to component (a) means a heavy fraction produced by catalytic cracking of heavy gas oil from the atmospheric or vacuum pipestill. This fraction suitably has a boiling point in the range from 184 to 376°C. This fraction is suitably present in the compositions of the present in an amount ranging from about 5-18 % by weight of the total fuel oil composition.

In the fuel oil composition of the present invention, the reference to component (b) means a gasoil product from an atmospheric pipestill which suitably has a boiling point in the range from about 244 to 330°C. This product is suitably present in the compositions of the present in an amount ranging from about 35-45% by weight of the total fuel oil composition.

The third essential component in the fuel oil compositions of the present invention is a light naphtha fraction (c) derived by the catalytic cracking of a heavy gasoil from an atmospheric or a vacuum pipestill. This naphtha fraction (c) suitably has a boiling point in the range from136 to 231°C and preferably component (a) and/or (b) in the fuel composition in an amount from about 5-15% by weight of the total composition. Fraction (c) suitably has an aromatics content in the range from about 60 - 75% by weight.

The fuel oil compositions of the present invention may contain in addition other conventional distillate fractions from a petroleum crude refinery process under atmospheric or vacuum conditions. These include *inter alia* components (d) to (g) described below:

(d) A fraction from a vacuum pipestill which suitably has a boiling point in the range from about 200 to 400°C, preferably from about 240-365°C. This fraction (d) is suitably present in the compositions of the present in an amount ranging from about 3-7% by weight, preferably from about 4-6 % by weight of the total composition.

(e) A fraction from an atmospheric pipestill which suitably has a boiling point in the range from about 160-380°C, preferably from about 183 to331°C. This fraction (e) is suitably present in the compositions of the present in an amount ranging from about 5 to 15% by weight, preferably from about 9 to 10% by weight, typically about 9.5-10.0% by weight.

(f) A fraction from an atmospheric pipestill which suitably has a boiling point in the range from about 230 -350°C, preferably from about 231 to 344°C. This fraction (f) is suitably present in the compositions of the present in an amount ranging from about 15 to 30% by weight, preferably from about 20-25% by weight.

(g) A fraction from an atmospheric pipestill which suitably has a boiling point in the range from about 210-420°C, preferably from about 216 to 395°C. This fraction is suitably present in the compositions of the present in an amount ranging from about 3 to 8% by weight, preferably from about 4-6 % by weight.

The fuel oil compositions of the present invention having an n-paraffin (C_{12+}) content of less than 20% by weight particularly benefit by blending with the light naphtha fraction (c). Such fuel oil compositions suitably have a cloud point of about -3 to -4°C.

The cold flow additive in fuel oil composition is suitably one that is generally available provided it is soluble in the fuel oil composition, although copolymers of

ethylene and at least one other unsaturated monomer which may be an additional mono-olefin or an unsaturated ester such as eg vinyl acetate, vinyl propionate, vinyl butyrate, ethyl acrylate and lauryl methacrylate or the like. The other unsaturated monomer can also be a mixture of an unsaturated mono-ester or diester and a straight chain or branched chain α-monoolefin. Mixtures of copolymers, such as eg a copolymer of ethylene and vinyl acetate with an alkylated polystyrene or with an acylated polystyrene, can also be used. Where the flow additive is a coolymer, it suitably consists of 1 to 40, preferably 1 to 20 and more preferably 3 to 20 molar proportions of ethylene per molar proportion of the other unsaturated monomer. The additive copolymer is suitably oil-soluble and has a number average molecular weight in the range from about 1,000 to 50,000, preferably about 1,000 to about 5,000. The cold flow additive is preferably an ethylene-vinyl carboxylate copolymer which may be selected from one or more of Paraflow®240, Paraflow® 226, Paraflow® 222, Paraflow® 275, Paraflow® 255, Paraflow® 223, Paraflow® 332, Paraflow® 209, Paraflow® 206, Paraflow® 480, Paraflow® 482, Paraflow® 479 (all ex Infineum), KF 6100S, KF 6100, KF 6301, KF 6101 (ex BASF), and DF 4842 (ex Clariant). Some of these oil-soluble additives which are eg olefin/vinyl carboxylate copolymers having a number average molecular weight as measured by vapour pressure osmometry of 1,000 to 10,000 which may optionally contain polar nitrogen compounds as co-additives, are described in EP-A-261957 and WO 94/00535.

The cold flow additive is suitably present in the oil composition in an amount from about 0.001-2.0% by weight of the total fuel oil composition.

The surprising feature of the present invention is that component (c), which is a relatively light fraction compared to the distribution of heavier components in fuel oils, is able to improve the effectiveness of conventional cold flow improvers in such fuel oils. It has been found that by using an aliquot of component (c) in the fuel oil compositions, it is possible to depress the cloud point and the temperature of operability, the latter as determined by the cold-filter plugging point (hereafter "CFPP") to a significant extent.

The present invention is further illustrated with reference to the following Examples:

EXAMPLES:

The following data was generated by subjecting a variety of fuel oils, each of which contained (i) 500 ppm by volume of an ethylene-vinyl acetate copolymer (Paraflow® 240, ex Infineum) cold flow additive and (ii) a 1050 ppm by volume of a gasoil marker dye, to a cold flow plugging point (CFPP) test. The test is described in detail in the text-book by Owen & Coley referred to above at pages 422-426 in Chapter 16.1.5. This is an IP 309 test and is also published as a European Standard by CEN, EN116:1981. Briefly, 40 ml of a sample of the test oil is cooled by a bath maintained at about -34°C. Periodically (at each 1°C drop in temperature starting from not less than 5°C above the cloud point thereof), the cooled oil is tested for its ability to flow through a fine screen in a given time period. This cold flow property is tested with a device consisting of a pipette the lower end of which is attached an inverted funnel positioned below the surface of the test oil. Stretched across the mouth of the funnel is a 350 mesh screen having an area of about 2.90 cm^2 (0.45 in^2). The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml. The test is repeated with each 1°C drop in temperature until the oil fails to fill the pipette up to that 20 ml mark within 60 seconds. The temperature at which the last filtration commenced is recorded as the CFPP.

TABLE

Components	Fuel Composition 1* (Wt %)	Fuel Composition 2 (Wt %)	Fuel Composition 3 (Wt %)
Component (g)	4.9	4.9	4.9
Component (e)	9.9	9.9	9.9
Component (a)	16.2	8.4	5.0
Component (c)	-	7.8	15.0
Component (b)	42.2	42.2	38.4
Component (f)	21.8	21.8	21.8
Component (d)	5.0	5.0	5.0
Total	100	100	100
Cloud point (°C)	-3	-4	-4
CFPP (°C)	-8	-10	-15

The above results show that partially replacing some of the conventional gas oil components in fuel oils with light naphtha fraction from the catalytic cracking of heavy gasoil clearly improves the CFPP of the fuel oils to a significant extent.